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(54) Multiphase steel and method for its production

(57) The invention relates to a high-strength steel sheet, which is uncoated or galvanized, and is characterized by a microstructure comprising ferrite and hardening structures, namely martensite, bainite, pearlite and/or residual austenite. The steel has a high work hardening index during static and dynamic deformation. The yield point:tensile strength ratio is low, both during

static and dynamic deformation, so that the steel is easy to work. The energy absorption during both static and dynamic deformation with 10-20% elongation is relatively high; it should be noted that 15% elongation is a typical value encountered in the event of a collision. The invention deals with high-strength cold-rolled steel for use in (automotive) components which are suitable for absorbing energy at high speed.

EP 1 154 028 A1

Description

[0001] The invention relates to multiphase steel and to its production.

[0002] In the automotive industry, there is an increasing demand for sheet steel which has a high strength and a high deformability, either galvanized or uncoated, in order to be able to produce more lightweight and safer cars.

[0003] High-strength steel can be obtained by using hardening mechanisms. Examples of known hardening mechanisms are ferrite grain refining, precipitation hardening (for example in high-strength low-alloy (HSLA) steel grades), structural hardening (for example in multiphase steel grades) and solid solution hardening (for example in phosphorus-containing (ultra)low carbon steel grades). The use of grain refining or solid solution hardening alone does not allow tensile strengths of 600 MPa or higher to be achieved. The drawback of precipitates and dissolved atoms is that the deformability of the steel is reduced. By contrast, multiphase steel satisfies the above requirements of a high strength in combination with a relatively high deformability.

[0004] Cold-rolled multiphase steel is produced by means of intercritical annealing in the two-phase austenite/ferrite range (the temperature range between Ac_1 and Ac_3), followed by cooling at a sufficiently high cooling rate to prevent the formation of pearlite, so that austenite is transformed into martensite or bainite during cooling and a ferritic/martensitic or ferritic/bainitic multiphase structure is obtained at room temperature.

[0005] To produce cold-rolled, ferritic/martensitic multiphase steel, the cooling rate after the annealing in the ferrite/austenite range has to be sufficiently high to prevent the formation of pearlite and bainite during the cooling. Elements such as Mn and Mo can be added, since they delay the formation of pearlite and bainite.

[0006] To obtain ferritic/bainitic multiphase steel, if appropriate with an additional quantity of 10-15% metastable austenite, the cooling rate after annealing has to be high enough to prevent the formation of pearlite. Moreover, a re-annealing treatment at generally 350-450°C is required for production of these steel grades, in order to transform austenite into bainite and to stabilize austenite. In addition to adding Mn, in order to prevent pearlite from forming during cooling, elements such as P, Si and Al should be added in order to stabilize austenite. The latter ferrite-forming and non-carbide-forming elements prevent precipitation of cementite and contribute to enriching the carbon content of austenite.

[0007] For automotive applications, it is generally desirable for the sheet steel to be galvanized. Immersion galvanization is preferred to electrolytic galvanization in view of the (process) costs. However, electrolytic galvanization has to be used if the steel is annealed by means of conventional bell-type annealing or on a conventional continuous annealing line which is only used to produce uncoated steel sheet. One possible advantage of electrolytic galvanization is that a better surface quality is obtained. Moreover, there are fewer problems caused by surface oxides during electrolytic galvanization, since they are removed by pickling prior to the galvanization process.

[0008] With the conventional immersion galvanization lines, the formation of hard martensite and bainite phases is only possible if relatively large quantities of the alloying elements Mn, Ni, Cr, Si, Al and Mo are added in order to prevent the formation of pearlite and the precipitation of cementite. This can be ascribed to the relatively low cooling rates of most immersion galvanization lines.

[0009] However, one drawback of this is that large quantities of these elements cause problems during casting and hot-rolling, which may cause process costs to mount up. Also, problems may occur during the welding of the steel. Moreover, during annealing Mn, Si and Cr may give rise to the formation of surface oxides, which has an adverse effect on the adhesion of the zinc and the surface quality after the immersion galvanization. In the case of electrolytic galvanization, the latter problem does not play a role, since the steel is pickled in advance.

[0010] It is an object of the invention to provide an improved multiphase steel with a high strength and good deformability. Another object of the invention is to provide a multiphase steel grade which can be produced successfully using the conventional process conditions. Yet another object of the invention is to provide a ferritic/martensitic and ferritic/bainitic multiphase steel which can be produced using the conventional continuous annealing lines and immersion galvanization lines. Yet another object of the invention is to provide a method for producing a multiphase steel of this type.

[0011] According to a first aspect of the invention, one or more of these objects is/are achieved with a multiphase steel having the following composition (in percent by weight unless otherwise indicated):

50 0.06 - 0.17% C

1.35 - 1.80% Mn

0.35 - 0.50% Si

0.02 - 0.12% P

55 0.05 - 0.50% Al

max. 0.07% Nb

max. 0.20% V

max. 0.05% Ti

max. 30 ppm B
 100 - 350 ppm N
 S, Cu, Sn, Ni, Cr, Mo as residual elements
 remainder Fe,

5 at least one of the elements P, Al, Nb, V, Ti, B and N being present, and the steel, after hot-rolling, finish-rolling, coiling at a customary temperature, and cold-rolling, being annealed, and the steel being hardened by a combination of structural hardening, grain refining, solid solution hardening and precipitation hardening, in order to obtain a high-strength cold-rolled steel.

10 [0012] The type and quantity of alloying elements are selected firstly on the basis of the expected effect on wetting during immersion galvanization and secondly on the basis of the maximum quantity possible under industrial process conditions (casting and rolling). Moreover, specific combinations have been taken into account: by way of example, a suitable combination of high Mn and Si contents may have a beneficial effect on the wetting during immersion galvanization.

15 [0013] In the multiphase steel according to the invention, the most important alloying element (other than carbon) is not molybdenum or chromium, but rather manganese. To prevent a poor surface quality, the quantity of manganese in the steel is no higher than 1.8%, which is too low to suppress the formation of pearlite under the cooling conditions encountered in many immersion galvanization lines. Therefore, small quantities of elements such as P, Al, Nb, V, Ti, B and N have been added. The choice of elements is based on the following metallurgical principles: (i) the prevention 20 of the formation of pearlite during cooling after annealing, and/or (ii) the promotion of grain refining, precipitation hardening and solid solution hardening of ferrite.

[0014] Preferably, the following are present in the multiphase steel according to the invention:

[0015] 0.02 - 0.07% Nb and/or 0.05 - 0.20% V and/or 0.03 - 0.05% Ti and/or 10-30 ppm B.

25 [0016] The use of the minimum quantities of Nb, V, Ti and/or B specified here means that in any event a larger quantity of these elements is used than the amount which would be present under normal conditions as residual elements in the steel.

[0017] Preferably, the following levels of the elements P, Al, Nb, V, Ti, B and N are present:

30 either 0.1 - 0.2% V,
 or 120 - 330 ppm N,
 or 0.02 - 0.07% Nb and 0.1 - 0.2% V,
 or 0.08 - 0.12% P and 15 - 30 ppm B,
 or 0.08 - 0.12% P, 15 - 30 ppm B and 0.03 - 0.05% Ti,
 or 0.08 - 0.12% P and 0.1 - 0.5% Al,
 35 or 0.08 - 0.12% P, 0.1 - 0.5% Al and 0.03 - 0.05% Ti,
 or 0.08 - 0.12% P, 0.1 - 0.5% Al, 0.03 - 0.05% Ti, 15 - 30 ppm B and 0.02-0.07% Nb.

[0018] The carbon content is preferably at least 0.08 - 0.10%, in order to form sufficient austenite during annealing. If there are elements which form carbide precipitates (Ti, Nb, V), the carbon content is preferably 0.16%.

40 [0019] The manganese content selected serves to counteract the formation of pearlite during cooling. Silicon ensures that ferrite is formed during annealing and cooling, with carbon remaining in austenite. The latter results in the stabilization of austenite.

[0020] Nitrogen can be added in order to stabilize austenite and for ferrite grain refining.

45 [0021] All these elements cause solution hardening to a greater or lesser extent, whether this be interstitial (nitrogen, carbon) or substitutional (phosphorus, manganese, silicon), resulting in hardening of the ferrite.

[0022] As a result of the addition of ferrite-forming elements which do not form carbides (silicon, aluminium and phosphorus), carbon remains in austenite during cooling, which results in stabilization of austenite. This is also dependent on the annealing process conditions (annealing temperature and time, cooling rate and re-annealing treatment).

50 [0023] Precipitation hardening of ferrite can be obtained by adding the elements Ti, Nb, V, Al and B with suitable quantities of C, S, N and P, in order to form precipitates. Although precipitation hardening is more effective in the hot-rolled state, it has an indirect effect on the strength after cold-rolling and annealing. The elements Ti and Nb are also added in order to form stable TiN and Nb(C, N) precipitates, so as to keep B and Al in solution, so that the latter elements can influence the transformation properties. Boron in solution prevents recrystallization of ferrite (resulting in grain refining) and is an element which promotes the formation of bainite.

55 [0024] Grain refining of austenite during the hot-rolling process can be obtained by adding niobium, since this element delays the growth of recrystallization nuclei. A smaller austenite grain in turn leads to a smaller ferrite grain and a higher austenite stability in the cold-rolled and annealed end product which is ultimately obtained.

[0025] The lower limit for the quantity of P, Al, Nb, V, Ti, B and N is determined by the quantity at which these elements remain active, while the upper limit is determined by the quantity at which the production process becomes impossible or too expensive.

[0026] According to a preferred embodiment, the steel has a microstructure which comprises ferrite and at least 15% of hardening structures of martensite, residual austenite and/or bainite, specifically at most 50% martensite and/or bainite.

[0027] Preferably, at most 50% hard phase (martensite and/or bainite) is present, in order to maintain sufficient elongation. If appropriate, at most 5-10% pearlite is present, provided that sufficient martensite and bainite are also present. The quantity of pearlite should preferably be low, since otherwise the multiphase properties, such as low $R_{p0.2\%}/R_m$ ratio and high tensile strength, are lost. In addition, it is also possible for there to be up to at most 10% residual austenite. Residual austenite is desirable, since in the metastable state it is plastically deformed, resulting in additional strength and elongation.

[0028] Preferably, the steel has a tensile strength of 600 - 1100 MPa. Consequently, the steel complies with the demand for high-strength steel from the automotive industry.

[0029] The steel preferably has a value of the product of tensile strength times total elongation (A_{80}) of from 12,000 - 25,000 MPa.%. This ensures a high strength and, at the same time, a high deformability.

[0030] The multiphase steel preferably has a yield point/tensile strength ($R_{p0.2\%}/R_m$) ratio of 0.4 to 0.6. This is favourable for the working properties during, for example, presswork. For the same reason, the steel preferably has a work hardening index of at least 0.165 and at most 0.30 between 10% elongation and uniform elongation.

[0031] According to a preferred embodiment, the work hardening index remains high and the $R_{p0.2\%}/R_m$ ratio, measured at a high rate of elongation of approximately 50 s^{-1} , remains lower than 0.7. A low $R_{p0.2\%}/R_m$ ratio of this nature (which corresponds to a high work hardening index) is favourable for steel which has to absorb energy in the event, for example, of a crash. A high work hardening index during rapid deformation also ensures that the deformation is spread across the material.

[0032] Preferably, the deformation energy of the multiphase steel, measured at a rate of elongation of approximately 50 s^{-1} and at elongation values of approximately 20%, is higher than the deformation energy of (ultra)low carbon steel (with or without solution hardening) and precipitation-hardened steel, and the deformation energy density is at least 250 mJ/mm³. Consequently, the steel will absorb relatively large amounts of energy in the event of rapid and high deformation, which is desirable under crash conditions in cars.

[0033] According to a preferred embodiment, the BH_2 index, which is defined by the yield point $R_{p0.2\%}$, measured after 2% prestretching and heating at 170°C for 20 minutes, minus the strength at 2% elongation (without prestretching and heating), is at least 55 MPa. This is considerably higher than the BH_2 of conventional "bake-hardening" steel grades (at most 30-40 MPa). A high BH_2 value means that the yield point increases relatively strongly after paint curing, which can provide a further weight saving.

[0034] According to a preferred embodiment, the surface of the steel is galvanized, either electrolytically galvanized or immersion galvanized. Consequently, the zinc protects the steel from corrosion, which is also desirable with a view to further coating (organic coating).

[0035] According to a second aspect of the invention, a method for producing multiphase steel as described above is provided, in which a slab of steel of the desired composition is produced, after which the slab is successively hot-rolled, finish-rolled, coiled and cold-rolled, and is then continuously annealed at a maximum annealing temperature of 760° - 820°C and is cooled at a rate of at most 100°C/s.

[0036] The hot-rolling parameters are selected in such a way that the steel in the hot-rolled state is sufficiently soft to be able to be cold-rolled. The said annealing temperature lies within the austenite/ferrite range, so that austenite is formed during annealing. By suitably selecting the cooling rate, austenite is converted into bainite and/or martensite during the cooling, depending on the composition, and the formation of pearlite is prevented.

[0037] According to a preferred embodiment, the cooling is carried out at a rate of 20-100°C/s on a continuous annealing line, after which a re-annealing treatment is carried out at a temperature of 250 - 470°C. With a continuous annealing line it is possible to achieve this cooling rate, while the re-annealing temperature is favourable for the transformation of austenite to bainite and for the stabilization of austenite.

[0038] The steel is preferably electrolytically galvanized after continuous annealing.

[0039] According to another preferred embodiment, the cooling is carried out at a rate of 5 to 50°C/s on an immersion galvanization line, during which process the surface of the steel is galvanized. With a conventional immersion galvanization line, the cooling can only be carried out at a lower rate than with a continuous annealing line, but immersion galvanization is more desirable than electrolytic galvanization in view of process costs.

[0040] The invention will be explained on the basis of a number of examples.

[0041] To investigate the chemical composition and annealing conditions required in order to obtain a minimum tensile strength level of approximately 600 MPa, various alloys with a basic composition of 0.16% C, 1.5% Mn and 0.39% Si and a further addition of the elements Ti, Nb, V, P, B, Al, N were annealed using a temperature/time profile

of conventional industrial immersion galvanization lines and continuous annealing lines.

[0042] Laboratory melts were produced (Table 1) with a 0.16% C, 1.5% Mn, 0.39% Si basic composition ("ref" in Table 1) and with varying quantities of N, B, Mn, V, Si, P, Al, Ti and Nb (steel codes A, B, C, D, E, F in Table 1). These elements are present in standard quantities, apart from cases where the quantities are shown in bold in Table 1.

5

Table 1:

| Steel composition (in percent by weight) of the steel grades examined | | | | | | | | | | |
|---|-------|--------------|--------------|--------------|--------------|--------------|--------------|-----------|--------------|------------|
| Code | C | Mn | P | Si | Al | Nb | V | B | Ti | N |
| | [%] | [%] | [%] | [%] | [%] | [%] | [%] | [ppm] | [%] | [ppm] |
| Ref | 0.156 | 1.508 | 0.012 | 0.376 | 0.037 | 0.001 | 0.001 | 1 | 0.002 | 44 |
| A | 0.167 | 1.510 | 0.007 | 0.391 | 0.036 | 0.002 | 0.107 | 1 | 0.008 | 80 |
| B | 0.158 | 1.703 | 0.006 | 0.485 | 0.045 | 0.001 | 0.004 | 1 | 0.004 | 330 |
| C | 0.157 | 1.764 | 0.111 | 0.516 | 0.089 | 0.053 | 0.006 | 21 | 0.040 | 38 |
| D | 0.157 | 1.503 | 0.011 | 0.818 | 0.043 | 0.002 | 0.001 | 1 | 0.005 | 34 |
| E | 0.162 | 1.522 | 0.007 | 0.398 | 0.043 | 0.051 | 0.001 | 1 | 0.004 | 34 |
| F | 0.161 | 1.503 | 0.097 | 0.398 | 0.032 | 0.002 | 0.005 | 20 | 0.023 | 32 |

[0043] For hot-rolling, blocks with dimensions of 60*100*40 mm were heated to 1250°C for 30 minutes. Hot rolling was carried out in six steps, starting from an initial thickness of 40 mm until a final thickness of 4 mm was reached. The finish-rolling temperature was 940-970°C and the simulated cooling temperature was 690 ± 10°C. After pickling, the hot-rolled material was cold-rolled, with a reduction of approximately 75%, to a final thickness of 1.1-1.2 mm.

[0044] The cold-rolled material was cut into sheets of approximately 550 x 120 mm, which were annealed on a continuous annealing simulator. The annealing process conditions (annealing temperature and time, heating rate and cooling rate, re-annealing treatment) were selected to correspond to those of conventional industrial immersion galvanization lines and continuous annealing lines (cf. the examples below).

30

Example 1: Multiphase steel produced on an immersion galvanization line with a low cooling rate

[0045] The steel grades given in Table 1 were annealed using parameters of an immersion galvanization line, with annealing carried out at a top temperature of 770-830°C, followed by slow cooling to 620-720°C, then cooling, at a rate V_Q of 7°C/s, to the temperature of the zinc bath. For the precise parameters, reference is made to Schedule 1 below.

35

Schedule 1: Process parameters (temperature, time, heating/cooling rate) of the immersion galvanization simulation of Example 1

40

[0046]

| V_{heat} | T_{top} | t_{anneal} | t_{sc} | T_Q | V_Q | T_{Zn} | t_{Zn} | V_{cool} |
|------------|-----------|--------------|----------|-------|--------|----------|----------|------------|
| [°C/s] | [°C] | [s] | [s] | [°C] | [°C/s] | [°C] | [s] | [°C/s] |
| 20 | 805 | 69 | 102 | 705 | 7 | 480-450 | 10.5 | 12 |

V_{heat} : heating rate; T_{top} : top temperature during annealing; t_{anneal} : annealing time; t_{sc} : period of slow cooling between top temperature and T_Q ; T_Q : temperature at which the rapid cooling begins; V_Q : cooling rate between T_Q and temperature of the zinc bath; T_{Zn} : temperature of the zinc bath; t_{Zn} : period for which the steel remains in the zinc bath; V_{cool} : cooling rate after the zinc bath (to 250°C).

45

[0047] The maximum annealing temperature T_{top} of 805°C lies within the austenite/ferrite range for all steel grades. This ensures that cementite and pearlite are transformed into austenite during the annealing.

50

[0048] Table 2 gives the mechanical properties for the annealed materials and compares them with those of the reference material.

Table 2:

Mechanical properties parallel to the rolling direction for material which has been annealed in accordance with the temperature/time profile of an immersion galvanization line with a cooling rate of 7°C/s. R_p : yield stress at 0.2% elongation; R_{eH} : upper yield point; R_{eL} : lower yield point; A_e : elastic elongation; R_m : tensile strength; A_u : uniform elongation; A_{80} : total elongation (elongation at break measured on a 20 x 80 mm European standard tensile specimen); n: work hardening index between 10% elongation and the uniform elongation

| Code | R_p | R_{eH} | R_{eL} | A_e | R_m | R_p/R_m | A_u | A_{80} | A_u/A_{80} | n | $R_m \times A_{80}$ |
|------|-------|----------|----------|-------|-------|-----------|-------|----------|--------------|-------|---------------------|
| | [MPa] | [MPa] | [MPa] | [%] | [MPa] | | [%] | [%] | | | [MPa.%] |
| ref | 404 | 414 | 390 | 1.8 | 583 | 0.69 | 17.2 | 24.8 | 0.69 | 0.173 | 14458 |
| A | 330 | 344 | 344 | | 634 | 0.52 | 14.2 | 15.0 | 0.95 | 0.192 | 9510 |
| B | 313 | | | | 673 | 0.47 | 17.4 | 21.1 | 0.82 | 0.202 | 14200 |
| C | 363 | | | | 843 | 0.43 | 14.0 | 16.5 | 0.85 | 0.176 | 13910 |
| D | 380 | 384 | 373 | 1.1 | 650 | 0.59 | 19.6 | 26.5 | 0.74 | 0.202 | 17225 |
| E | 454 | 469 | 449 | 3.0 | 593 | 0.77 | 16.9 | 25.3 | 0.67 | 0.175 | 15003 |
| F | 371 | 375 | 367 | 1.2 | 662 | 0.56 | 19.0 | 25.8 | 0.74 | 0.209 | 17080 |

[0049] Table 3 shows the structural properties of the annealed materials. In this context, it should be pointed out that a relatively small ferrite grain was found for steel E, which is to be expected for this Nb-containing variant.

Table 3:

| Structural properties of the annealed materials. Type of second phase present and surface fractions of pearlite + bainite + any carbides (P+B), martensite and/or residual austenite (M+RA), and residual austenite (RA). | | | | |
|---|---------------------|-----|------|-----|
| Steel code | Type of 2nd phase | B+P | M+RA | RA |
| Ref | P | 15 | 0 | 0.6 |
| A | M/RA+B | 6 | 6 | 2.6 |
| B | M/RA (+ a little B) | 3 | 17 | 4.4 |
| C | M/RA | 0 | 14 | 2.8 |
| D | M/RA+B | 9 | 12 | 3.7 |
| E | B+P | 9 | 1 | 1.0 |
| F | M/RA+B | 8 | 10 | 3.0 |

[0050] If the mechanical properties are compared with the microstructure, it is noticeable that steel grades with a second phase comprising virtually exclusively martensite (steel codes B and C) have the highest tensile strength (> 670 MPa) and the lowest $R_{p0.2\%}/R_m$ ratio (0.4-0.5). These steel grades show a continuous yielding behaviour. The absence of a yield point elongation is typical for ferritic/martensitic multiphase steel.

[0051] For steel grades with a tensile strength of between 600-670 MPa and an $R_{p0.2\%}/R_m$ ratio of between 0.5-0.65, a low elastic limit was found ($A_e < 1.5\%$) (steel codes A, D and F). The second phase of these steel grades comprises primarily martensite, bainite and a little residual austenite.

[0052] The presence of an elastic limit ($A_e > 1.5\%$), a relatively high $R_{p0.2\%}/R_m$ ratio (> 0.65) and a tensile strength of lower than 600 MPa correlates with primarily pearlite (P) being present as the second phase (steel codes ref and E). These mechanical properties are the direct consequence of the presence of predominantly pearlite as the second phase. It is clear from this that pearlite is unfavourable for the mechanical properties.

[0053] It can be seen from Tables 2 and 3 that the desired properties, i.e. a tensile strength of higher than 600 MPa, an $R_{p0.2\%}/R_m$ ratio of lower than 0.6, a low elastic limit and a ferritic/bainitic or ferritic/martensitic structure, are obtained for all compositions under the given annealing conditions, with the exception of steel codes ref and E.

[0054] On the basis of the mechanical properties of steel A (V-containing variant) and E (Nb-containing variant), it is to be expected that if a combination of Nb, which provides grain refining, and V, which promotes the formation of

martensite, is added, the mechanical properties can be improved considerably.

[0055] However, the product of total strength times total elongation of at least 12,000 MPa.% is not achieved for steel A, although it is to be expected that for steel A produced under industrial conditions the total elongation A_{80} will be higher; this is because the structure for industrially produced steel is generally higher than for laboratory-produced steel.

Example 1a: Properties during ageing and paint curing

[0056] With the exception of steel E, the steel grades display a relatively high increase in the yield stress after a paint curing simulation following annealing as described in Example 1. A simulation of this nature comprises 2% pre-stretching of the annealed material followed by "paint curing" (annealing) for 20 minutes at 170°C. From this example too, it is clear that steel E does not have typical multiphase properties, which is the direct consequence of the ferritic/pearlitic structure of this steel. The BH₂ index is given in Table 4. The BH₂ index is defined as: $BH_2 = R_{p0.2\%} / (R_p + \Delta R_p)$ (after 2% prestretching and "paint curing" for 20 minutes at 170°C) minus the strength at 2% elongation (in the annealed state).

Table 4:

| Increase in strength as a result of 2% stretching and annealing at 170°C for 20 minutes. The bake-hardening index is given in the final column. | | | | | |
|---|--------------|--------------|--------------|--------------|--------|
| Code | ΔR_p | ΔR_p | ΔR_m | ΔR_m | BH_2 |
| | [MPa] | [rel, %] | [MPa] | [rel, %] | [MPa] |
| A | 148 | 49 | 30 | 5 | 64 |
| B | 198 | 63 | 46 | 7 | 71 |
| C | 272 | 75 | 63 | 7 | 83 |
| D | 106 | 28 | 31 | 5 | 83 |
| E | 18 | 4 | 20 | 3 | 1 |
| F | 106 | 29 | 32 | 5 | 85 |

[0057] Even after this paint curing simulation, no elastic limit is detected for steels B and C. An elastic limit is only detected if an elastic limit is already present in the annealed state (cf. Table 2), which is the case for steels A, D and E.

[0058] The abovementioned annealed steel grades from Example 1 do not appear to be sensitive to annealing for two hours at 100°C, which represents a conventional simulation of natural ageing.

[0059] The low tendency to natural ageing and the good bake-hardening properties are typical of in particular ferritic/martensitic multiphase steel grades which contain little carbon in solution.

Example 1b: Sensitivity to rate of elongation (IDEM)

[0060] To gain some idea of the ability of the abovementioned annealed steel grades from Example 1 to withstand crashes, the mechanical properties were determined at different rates of elongation between 0.001 and 100 s⁻¹. The deformation energy absorbed as a function of the elongation can be calculated by determining the area below the tension elongation curves. In this way, the deformation energy absorbed was determined up to an elongation of 5% and 20% both with a low rate of elongation (0.001 s⁻¹) and with a high rate of elongation (50 s⁻¹). Fig. 1 plots the deformation energy against the static yield stress.

[0061] If the deformation energy (with respect to the static yield stress) of steel grades A to F is compared with that of other industrially produced (ultra)low carbon steel (IF, LC in Fig. 1), HSLA steel and steel grades hardened by means of solution hardening (P-IF and P-LC in Fig. 1), the deformation energy of steels A-F and for other ferritic/martensitic multiphase steel grades (DP and ref3 in Fig. 1) at 20% deformation proves to be higher to a greater or lesser extent than for the other steel grades. This applies in particular when high rates of elongation (50 s⁻¹) are used.

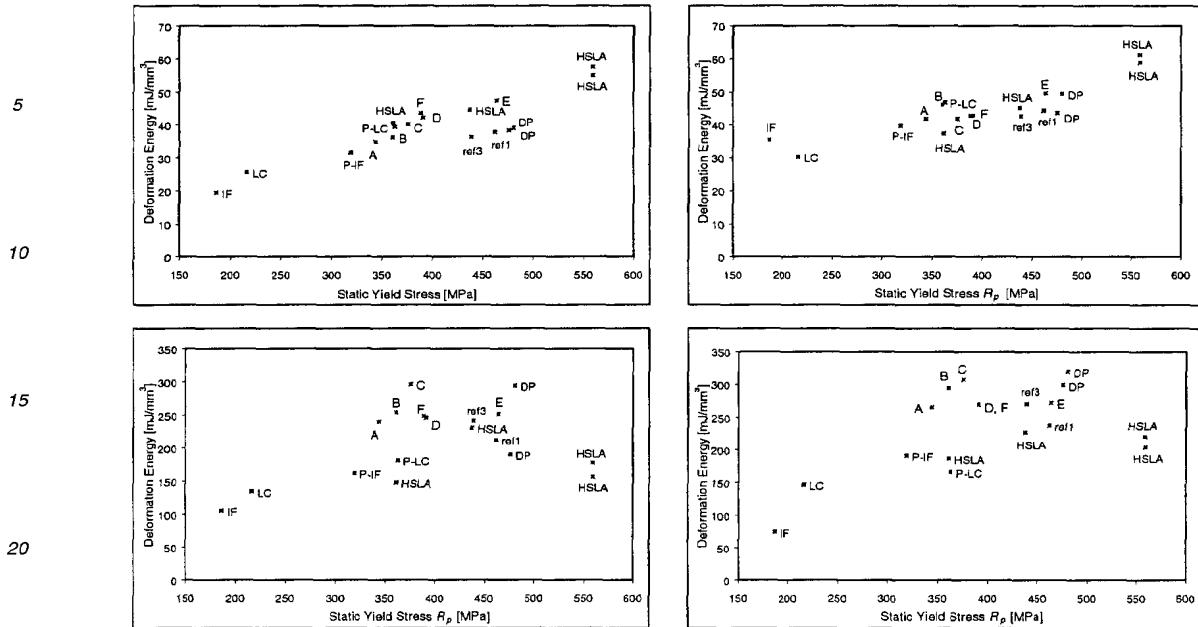


Fig. 1: Deformation energy density at a low rate of elongation of 0.001 s^{-1} (on the left) and a high rate of elongation of 50 s^{-1} (on the right). Top: 5% elongation; bottom: 20% elongation.

[0062] The difference between steels A-F (and DP) and the other steel grades must be attributed to the difference in microstructure: the multiphase steel grades contain relatively large amounts of second phase structures, such as bainite and martensite, while the other steel grades consist only of ferrite or ferrite with a little pearlite. For steel ref (ref1 in Fig. 1), comprising a pure ferritic/pearlitic structure, the deformation energy is lower than for ferritic/martensitic and ferritic/bainitic steel grades.

[0063] The major advantage of multiphase steel compared to the other steel grades is that the work hardening index is relatively high and remains high even for high rates of elongation. This is expressed by the $R_{p0.2\%}/R_m$ ratio, which for the multiphase steel grades examined remains below 0.7 even at high rates of elongation, while the $R_{p0.2\%}/R_m$ ratio increases considerably at an increasing rate of elongation for the other steel grades.

Example 2: Multiphase steel produced on an immersion galvanization line with a cooling rate of 20°C/s

[0064] The second example relates to a simulation of an immersion galvanization line in which, unlike in Example 1, there is no slow cooling after annealing: the material is cooled directly from the maximum annealing temperature (820°C) to the temperature of the zinc bath ($480\text{--}450^\circ \text{C}$). The cooling rate during cooling to the galvanization temperature is 20°C/s , i.e. considerably higher than the 7°C/s used in Example 1 (cf. Schedule 2 below). The mechanical properties are summarized in Table 5 for steels A to F.

Schedule 2: Process parameters (temperature, time, heating/cooling rate) of the immersion galvanization simulation from Example 2.

[0065]

| V_{heat} [$^\circ \text{C/s}$] | T_{top} [$^\circ \text{C}$] | t_{anneal} [s] | t_{Sc} [s] | T_Q [$^\circ \text{C}$] | V_Q [$^\circ \text{C/s}$] | T_{Zn} [$^\circ \text{C}$] | t_{Zn} [s] | V_{cool} [$^\circ \text{C/s}$] |
|---|--|-------------------------|---------------------|-----------------------------|-------------------------------|---------------------------------------|---------------------|---|
| 21 | 820 | 61 | - | - | 20 | 470-450 | 9.7 | 13 |

V_{heat} : heating rate; t_{anneal} : top temperature during annealing; T_Q : temperature at which the rapid cooling begins, in this case equal to T_{top} ; V_Q : cooling rate between T_Q and the temperature of the zinc bath; T_{Zn} : temperature of the zinc bath; t_{Zn} : time for which the steel remains in the zinc bath; V_{cool} : cooling rate to 250°C after the zinc bath.

Table 5:

| Code | R_p | R_{eH} | R_{eL} | A_e | R_m | R_p/R_m | A_u | A_{80} | A_u/A_{80} | n | $R_m \times A_{80}$ |
|------|-------|----------|----------|-------|-------|-----------|-------|----------|--------------|-------|---------------------|
| | [MPa] | [MPa] | [MPa] | [%] | [MPa] | | [%] | [%] | [%] | | [MPa.%] |
| A | 310 | | | | 670 | 0.46 | 16.0 | 19.9 | 0.81 | 0.199 | 13333 |
| B | 321 | | | | 701 | 0.46 | 17.9 | 22.1 | 0.81 | 0.202 | 15492 |
| C | 356 | | | | 858 | 0.41 | 15.4 | 19.1 | 0.81 | 0.186 | 16388 |
| D | 349 | 351 | 348 | 0.7 | 675 | 0.52 | 21.0 | 26.1 | 0.80 | 0.237 | 17618 |
| E | 435 | 438 | 426 | 1.9 | 638 | 0.68 | 14.5 | 17.0 | 0.85 | 0.180 | 10846 |
| F | 334 | 337 | 335 | 0.5 | 689 | 0.48 | 19.4 | 23.8 | 0.81 | 0.224 | 16398 |

[0066] The higher cooling rate means that the mechanical properties are considerably improved compared to Table 1: in this case, multiphase properties are obtained for all the steel grades examined, with the exception of steel E (Table 5). This is clear from the relatively high tensile strength, the lower $R_{p0.2\%}/R_m$ ratio and the decrease in the elastic limit compared to Example 1 (compare Tables 2 and 5). These mechanical properties correspond to a second phase which is characterized by substantially martensite and bainite. The higher cooling rate ensures that less pearlite is formed during cooling.

Example 3: Continuous annealing line with re-annealing treatment

[0067] The last example simulated an existing continuous annealing line in which the steel is annealed for 30 seconds at a maximum temperature of 760-840°C, followed by slow cooling to a temperature T_Q of 620-720°C. This slow cooling is followed by rapid cooling at approximately 50-100°C/s to the re-annealing temperature (250-470°C) and then a re-annealing treatment for 1-3 minutes.

[0068] A re-annealing treatment of this type is favourable for transforming austenite into bainite. During this isothermal bainite transformation, austenite is enriched with carbon, resulting in stabilization of austenite. At a lower re-annealing temperature or with a shorter re-annealing period, in relative terms more hard second phase (martensite and bainite) will be obtained, while at high re-annealing temperatures (470°C) or with longer re-annealing periods, pearlite may also be formed and cementite may be precipitated. Pearlite and cementite are undesirable, since they are unfavourable for the mechanical properties, as is also clear from the above examples. However, the formation of pearlite and the precipitation of cementite are dependent on the composition: the more non-carbide-forming elements (Si, P, Al) are added, the higher the re-annealing temperature can be. This is because these elements tend to prevent the precipitation of cementite.

[0069] For an annealing temperature of 800°C, a T_Q of 660°C, a re-annealing temperature of 400°C and a re-annealing period of 1 minute (cf. Schedule 3), the mechanical properties are given in Table 6.

Schedule 3: Process parameters (temperature, time, heating/cooling rate) of the continuous annealing simulation of Example 3.

[0070]

| V_{heat} | T_{anneal} | t_{anneal} | t_{SC} | T_Q | V_Q | $T_{re-anneal}$ | $t_{re-anneal}$ | V_{cool} |
|------------|--------------|--------------|----------|-------|--------|-----------------|-----------------|------------|
| [°C/s] | [°C] | [s] | [s] | [°C] | [°C/s] | [°C] | [s] | [°C/s] |
| 30 | 800 | 30 | 30 | 660 | 100 | 400 | 60 | 50 |

V_{heat} : heating rate; T_{anneal} : top temperature during annealing; t_{SC} : period of slow cooling between top temperature and T_Q ; T_Q : temperature at which the rapid cooling begins; V_Q : cooling rate between T_Q and re-annealing temperature; $T_{re-anneal}$: re-annealing temperature; $t_{re-anneal}$: duration of the re-annealing treatment; V_{cool} : cooling rate to room tem-

perature after re-annealing.

Table 6:

| Mechanical properties parallel to the rolling direction for steel which has been annealed in accordance with the temperature/time cycle of a continuous annealing line with a selected annealing temperature of 800°C and re-annealing temperature of 400°C. | | | | | | | | | | | | |
|--|----------------|-----------------|-----------------|----------------|----------------|--------------------------------|----------------|-----------------|---------------------------------|-------|---------------------------------|--|
| Code | R _p | R _{eH} | R _{eL} | A _e | R _m | R _p /R _m | A _u | A ₈₀ | A _u /A ₈₀ | n | R _m xA ₈₀ | |
| | [MPa] | [MPa] | [MPa] | [%] | [MPa] | | [%] | [%] | | | [MPa.%] | |
| ref | 344 | | | | 651 | 0.53 | 15.0 | 19.6 | 0.77 | 0.182 | 12760 | |
| A | 337 | | | | 694 | 0.49 | 14.0 | 18.0 | 0.78 | 0.175 | 12492 | |
| B | 331 | | | | 719 | 0.46 | 13.1 | 16.4 | 0.80 | 0.166 | 11792 | |
| C | 410 | | | | 863 | 0.47 | 13.2 | 15.1 | 0.87 | 0.163 | 13031 | |
| D | 331 | | | | 720 | 0.46 | 17.5 | 20.5 | 0.85 | 0.209 | 14760 | |
| E | 430 | | | | 681 | 0.63 | 15.9 | 19.2 | 0.83 | 0.193 | 13075 | |
| F | 352 | | | | 697 | 0.50 | 15.4 | 18.7 | 0.82 | 0.176 | 13034 | |

[0071] The much higher tensile strengths than in Examples 1 and 2 are noticeable. This is the direct consequence of a higher cooling rate, so that there can be little to no pearlite formation for the steel compositions in question. Therefore, an elastic limit was also not found for any of the steel grades.

[0072] The sensitivity of ref to the rate of elongation is also considerably improved (ref3 in Fig. 1). Therefore, the steel comprises predominantly ferrite and martensite, with a little bainite. On the basis of the mechanical properties (R_{p0.2%}/R_m ratio, tensile strength) of the remaining steel grades A-F, which are even better than those of the reference material (cf. Table 6), it can be expected that the sensitivity of steels A-F to the rate of elongation will be higher than that of steel ref, since, after all, they have the same basic composition.}

[0073] For steel ref, it has been found that a lower re-annealing temperature of 300°C still considerably improves the mechanical properties. The tensile strength increases by almost 100 MPa, from 651 MPa to 744 MPa, while the R_{p0.2%}/R_m ratio falls from 0.53 to 0.42 (the total elongation and the N value remaining constant). This is the consequence of the presence of more martensite, in relative terms, compared to bainite if the steel is re-annealed at lower temperatures. For steels A-F, with the same basic composition, it is also possible to expect a much higher tensile strength if the steel is annealed at a lower temperature.}

[0074] A possible drawback of a continuous annealing line is that the end product is not directly galvanized, as is the case on an immersion galvanization line after annealing. However, if coated steel sheet is desired, the steel can be electrolytically galvanized after the annealing.

Claims

1. Multiphase steel having the following composition (in percent by weight unless otherwise indicated):

0.06 - 0.17% C
 1.35 - 1.80% Mn
 0.35 - 0.50% Si
 0.02-0.12% P
 0.05 - 0.50% Al
 max. 0.07% Nb
 max. 0.20% V
 max. 0.05% Ti
 max. 30 ppm B
 100 - 350 ppm N
 S, Cu, Sn, Ni, Cr, Mo as residual elements
 remainder Fe,

at least one of the elements P, Al, Nb, V, Ti, B and N being present, and the steel, after hot-rolling, finish-rolling, coiling at a customary temperature, and cold-rolling, being annealed, and the steel being hardened by a combination of structural hardening, grain refining, solid solution hardening and precipitation hardening, in order to obtain a high-strength cold-rolled steel.

5 2. Multiphase steel according to Claim 1, in which the following are present:
0.02 - 0.07% Nb and/or 0.05 - 0.20% V and/or 0.03 - 0.05% Ti and/or 10-30 ppm B.

10 3. Multiphase steel according to Claim 1 or 2, in which the following levels of the elements P, Al, Nb, V, Ti, B and N, are present:

either 0.1 - 0.2% V,
or 120 - 330 ppm N,
or 0.02 - 0.07% Nb and 0.1 - 0.2% V,
15 or 0.08 - 0.12% P and 15 - 30 ppm B,
or 0.08 - 0.12% P, 15 - 30 ppm B and 0.03 - 0.05% Ti,
or 0.08 - 0.12% P and 0.1 - 0.5% Al,
or 0.08 - 0.12% P, 0.1 - 0.5% Al and 0.03 - 0.05% Ti,
20 or 0.08 - 0.12% P, 0.1 - 0.5% Al, 0.03 - 0.05% Ti, 15 - 30 ppm B and 0.02-0.07% Nb.

25 4. Multiphase steel according to Claim 1, 2 or 3, in which the steel has a microstructure which comprises ferrite and at least 15% of hardening structures of martensite, residual austenite and/or bainite, specifically at most 50% martensite and/or bainite and at most 10% residual austenite, and optionally at most 5-10% pearlite.

30 5. Multiphase steel according to one of the preceding Claims, which has a tensile strength of 600 - 1100 MPa.

35 6. Multiphase steel according to one of the preceding Claims, in which the value of the product of tensile strength times total elongation (A_{80}) is from 12,000-25,000 MPa.%.

40 7. Multiphase steel according to one of the preceding Claims, which has a yield point/tensile strength ($R_{p0.2\%}/R_m$) ratio of 0.4 to 0.6.

45 8. Multiphase steel according to one of the preceding Claims, in which the work hardening index remains high and the $R_{p0.2\%}/R_m$ ratio, measured at a high rate of elongation of approximately 50 s^{-1} , remains lower than 0.7.

50 9. Multiphase steel according to one of the preceding Claims, which has a work hardening index of at least 0.165 and at most 0.30 between 10% elongation and uniform elongation.

55 10. Multiphase steel according to one of the preceding Claims, in which the deformation energy density, measured at a rate of elongation of approximately 50 s^{-1} and at elongation values of approximately 20%, is higher than the deformation energy density of (ultra)low carbon steel and precipitation-hardened steel, and is at least 250 mJ/mm³.

60 11. Multiphase steel according to one of the preceding Claims, in which the BH₂ index, which is defined by the yield point $R_{p0.2\%}$, measured after 2% prestretching and then heating at 170°C for 20 minutes, minus the strength at 2% elongation (without prestretching and/or heating), is at least 55 MPa.

65 12. Multiphase steel according to one of the preceding Claims, in which the surface of the steel is galvanized, preferably electrolytically galvanized or immersion galvanized.

70 13. Method for producing multiphase steel according to one of the preceding Claims, in which a slab of steel of the desired composition is produced, after which the slab is successively hot-rolled, finish-rolled, coiled and cold-rolled, and is then continuously annealed, at a maximum annealing temperature of 760° - 820°C, and is cooled at a rate of at most 100°C/s.

75 14. Method according to Claim 13, in which the cooling is carried out at a rate of 20-100°C/s on a continuous annealing line, after which a re-annealing treatment is carried out at a temperature of 250 - 470°C.

80 15. Method according to Claim 14, in which the steel surface is electrolytically galvanized.

16. Method according to Claim 13, in which the cooling is carried out at a rate of 5 to 50°C/s on an immersion galvanization line, during which process the steel surface is galvanized.

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EUROPEAN SEARCH REPORT

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